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White Patchy Materials Formed in a Scoriaceous Road-cut Profile on Miyake Island

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Summary

Sulfurous gas, sulfur or sulfates are frequently contained in volcanic ejecta. We found white patchy materials (WPM) in a road-cut profile on Miyake Island, Japan. The layer containing WPM consists of scoria deposit in 1874. The major materials we identified in the WPM were $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and amorphous silica according to X-ray diffraction and energy dispersive X-ray analyses. A possible process for crystallization of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the WPM is the dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ contained in the overlying 2000 ash and its re-precipitation on the surface of the scoriaceous road-cut profile. Emission of sulfur dioxide gas, converted to sulfuric acid in water, has been so abundant since the 2000 eruption that we further examined reaction products between crushed scoria and dilute H_2SO_4 (0.1–2.5 mol L⁻¹). $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was also identified in the reaction products as well as alunogen, iron sulfate, etc. Because alunogen is highly soluble in water, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was the major crystalline product after rinsing with water.

Key words : Scoria, volcanic gas, gypsum, SEM, Miyake-jima

Miyake Island is an active volcano in the Izu island chain, Japan. It is located near the northern rim of the Philippine Sea Plate. It has erupted more than 10 times since the 15th century. The volcanic ejecta on Miyake Island are mostly basaltic materials such as lava flow and scoria deposits. Scoria deposits of different ages are distributed at different places on the island (Kato et al., 2005). A large amount of sulfur dioxide gas has been emitted from the central crater area on the island since the 2000 eruption. The sulfur content of the 2000 ash was also high (20–45 g S kg⁻¹) (Yazawa et al., 2002). The damage to vegetation due to the gas is evident at many places (Yamanishi et al., 2003). Areas with a high sulfur dioxide concentration are dependent on the wind direction.

Under the humid temperate climate on the island, the lava flow and scoria deposits gradually weather, and an Al-humus complex, allophane, imogolite, and ferrihydrite are being formed with time (Kato *et al.*, 2005) in the usual volcanic ash soil formation process (Shoji *et al.*, 1993). However, sulfur dioxide gas may produce additional weathering products from scoria on Miyake Island. We found white patchy materials (WPM) in a scoriaceous road-cut soil profile.

Delfosse (2005) and Delfosse *et al.* (2006) reported that basic aluminum sulfate (BAS) formed with acidic sulfur gas in Nicaragua using energy dispersive X-ray (EDX) analysis, although it was found in the clay fraction. This was the first finding that BAS formed under natural conditions. The relationship between BAS (Adams and Rwajfih, 1977; Agbenin, 2003) and the WPM in the road-cut profile on Miyake Island was another point of interest.

The objectives of this study were (i) to identify the materials present in the WPM in the road-cut profile and (ii) to compare the WPM and the products formed with sulfuric acid treatment of the scoria.

Materials and Methods

The WPM was found in the scoriaceous road-cut profile on August 25th, 2007 at site No. 4 reported by Kato *et al.* (2005), Miyake Island (Fig. 1-i). The scoria deposit was loose enough to sample WPM using a trowel. Kato *et al.* (2005) described the morphological properties of the road-cut soil profile. The scoria was deposited in 1874. The WPM and the surface of the scoria deposits were dry on the sampled day.

The WPM appeared to consist of two constituents under an optical microscope (Fig. 1-ii). Prismatic transparent crystals tended to locate on the outer

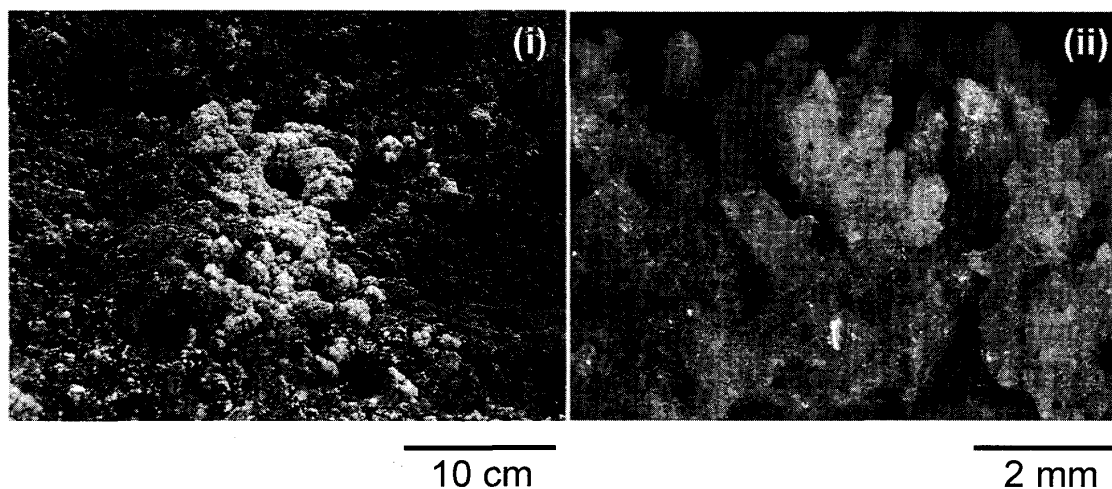


FIG. 1. (i) White patchy materials (WPM) found in the road-cut profile of 1874 scoria, Miyake Island. (ii) Optical microscopic image of WPM.

side. White powdery precipitates existed between the prismatic crystals and the scoria surface and also in pores inside the scoria deposit. The prismatic crystals were scarce in the pores inside the scoria. The prismatic crystals and the powdery precipitates were ground in an agate mortar and provided for X-ray diffraction (XRD) analysis. XRD patterns were obtained using a Rigaku Miniflex at a lamp current of 30 mA and 15 kV.

Portions of the prismatic crystals and the powdery precipitates were placed on the sample holder for the scanning electron microscope (SEM) using double-sided sticky tape and were coated with vacuum-evaporated carbon. SEM observation was done using a Hitachi S4200 operated at 15 kV. EDX analysis was conducted using a Kevex X-ray microprobe equipped with a SEM.

In order to compare the WPM with the reaction product of scoria and dilute sulfuric acid, a fresh part of the scoria was crushed to pass through a 2-mm sieve using an agate mortar. A simple small reaction vessel was prepared using a 5-mL auto-pipette tip and a balled-up plastic string. The balled-up plastic string was set at a depth of 1.5 cm inside the auto-pipette tip and used as a water-permeable holder for the scoria. A 1.5 g portion of the crushed scoria was placed on the balled-up plastic string inside the pipette tip as shown in Fig. 4. On the surface of the scoria in each reaction vessel, 0.5 mL of water, 0.1, 0.5 and 2.5 mol L⁻¹ sulfuric acid aqueous solution was added drop by drop using a pipette and allowed to stand at room temperature. All the solutions were held in the scoria layer with no drainage through the plastic string ball. After 4 days, the upper part of the scoria was sampled with a knife and used for XRD and SEM-EDX analyses as described above. To remove water-soluble materials, a few drops of water was added to a small amount of sample on a watch glass and then the water was absorbed to a paper wiper through its edge. After repeating this water rinse 5 times, the dried sample was used for additional XRD and SEM-EDX analyses. The remaining part of the scoria was moved to a plastic test tube and the pH(H₂O) was determined using a glass electrode one hour after addition of a 3.75 mL pure water and shaking.

Results and Discussion

The WPM on the road-cut profile of scoria deposit

At least two materials were identified in the WPM. One was CaSO₄ · 2H₂O and the other was amorphous silica. The XRD patterns are shown in Fig. 2. Intense diffraction peaks were obtained from WPM rich in prismatic crystals. The major peaks at 0.758, 0.425, 0.376 and 0.305 nm were identified as those from CaSO₄ · 2H₂O (Fig. 2a). In contrast, no strong diffraction peak was obtained from the white powdery precipitate. Although several weak diffraction peaks were observed, they are attributable to small amount of feldspar in the scoria

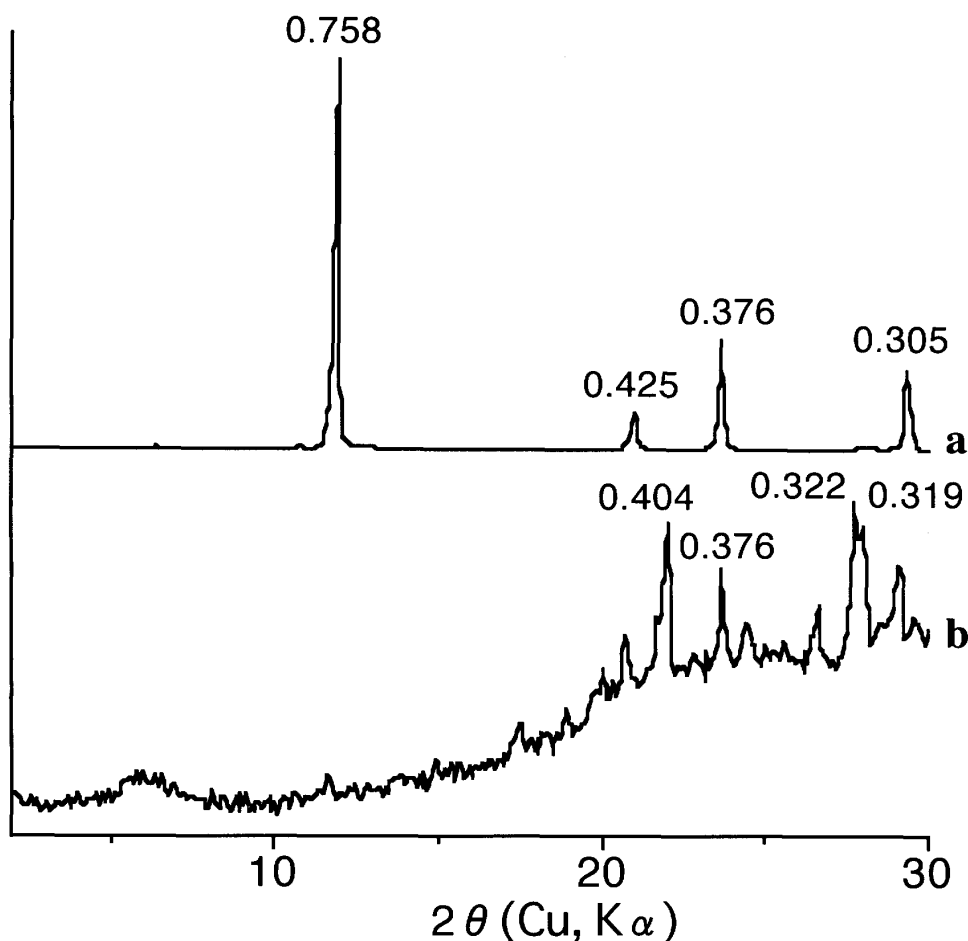


FIG. 2. a: X-ray diffraction (XRD) pattern of crystalline white patchy materials found in the road-cut profile of the 1874 scoria, Miyake Island. b: XRD pattern of a white powdery precipitate obtained from pores in scoria.

(Fig. 2b). Among the weak diffraction peaks in Fig. 2b, a peak at 0.404 nm may be attributable to cristobalite (Brown, 1980) because the white powdery precipitate consists mostly of silica as mentioned below, and the peak intensity at 0.404 nm is stronger than that at 0.32 nm, usually the strongest diffraction peak among those due to feldspar.

Identification of these materials was supported by SEM-EDX analyses. Fig. 3 shows a SEM image and element maps (Ca, S and Si) of an intermingled part of the WPM. The SEM image indicates that WPM consists of prismatic crystals and an amorphous material. The prismatic crystals are rich in Ca and S according to the element maps, and the EDX spectrum suggests that the atomic ratio of Ca : S is approximately 1 : 1 (Fig. 3a). Thus, the prismatic crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were also supported by SEM-EDX analyses. On the other hand, the amorphous precipitate consists mostly of Si according to the element maps (Fig. 3) and the EDX spectrum (Fig. 3b). The silica precipitate may include cristobalite accord-

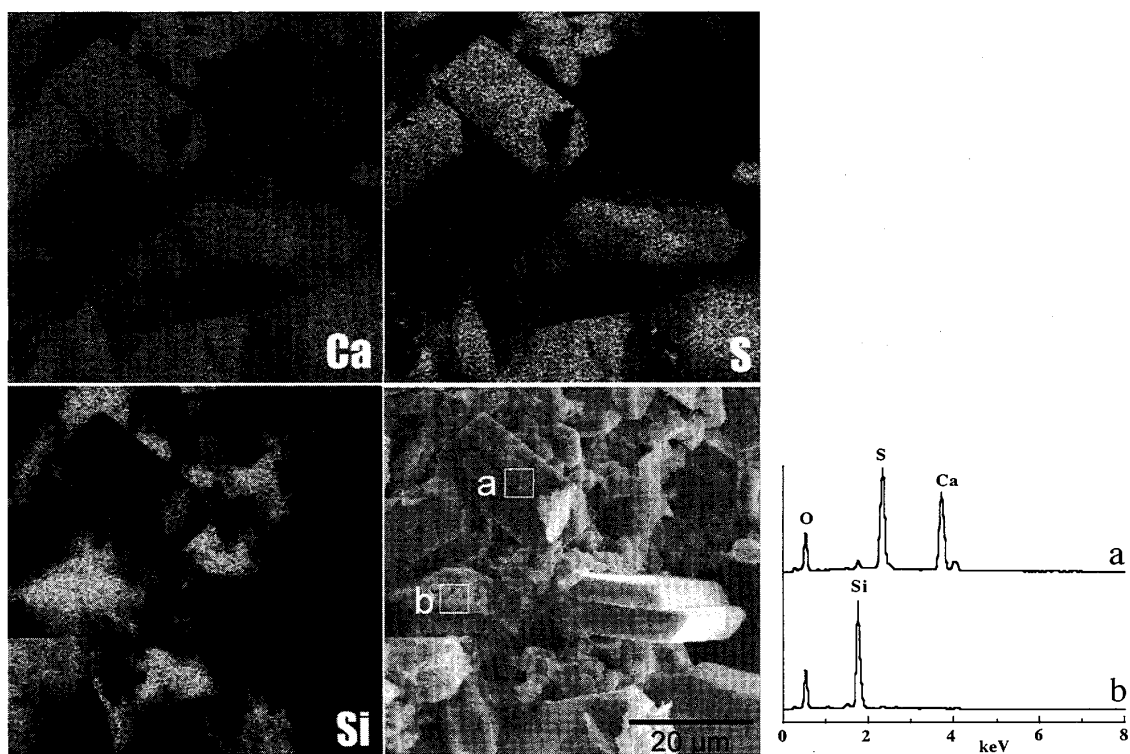


FIG. 3. Element maps for Ca, S and Si and a SEM image of white patchy materials in the road-cut profile of scoria on Miyake Island. Energy dispersive X-ray spectra of selected areas a and b in the SEM image are also shown on the right hand side.

ing to the XRD pattern as mentioned above.

Reaction products formed on the surface of scoria with the addition of dilute sulfuric acid

On the surface of the scoria with added H_2SO_4 , a white material started to appear one or two days after the addition of H_2SO_4 . The amount of the white material appeared abundant on the scoria to which 0.5 M H_2SO_4 was added (Fig. 4). The scoria with added 0, 0.1 and 0.5 M H_2SO_4 was parched 4 days after H_2SO_4 addition, and the surface of the scoria on which 0.1 and 0.5 M H_2SO_4 was added became hard. The scoria, on which 2.5 M H_2SO_4 was added, appeared wet on the 4th day after the addition of H_2SO_4 and crystalline materials formed on the surface. Possible reasons are the hydration of unreacted H_2SO_4 , covering of the scoria surface with transparent crystalline materials, etc.

The XRD patterns in Fig. 5 indicate that crystalline products formed with the addition of H_2SO_4 . The diffraction peaks at 0.405, 0.376, 0.364, 0.32 and 0.302 nm (Fig. 5a) are due to feldspar in the scoria. With the addition of H_2SO_4 , diffraction peaks appeared at 1.34, 0.448, 0.438, 0.427, etc., are evident in Fig. 5c and d, but weak in Fig. 5b. These diffraction peaks are attributable to alunogen

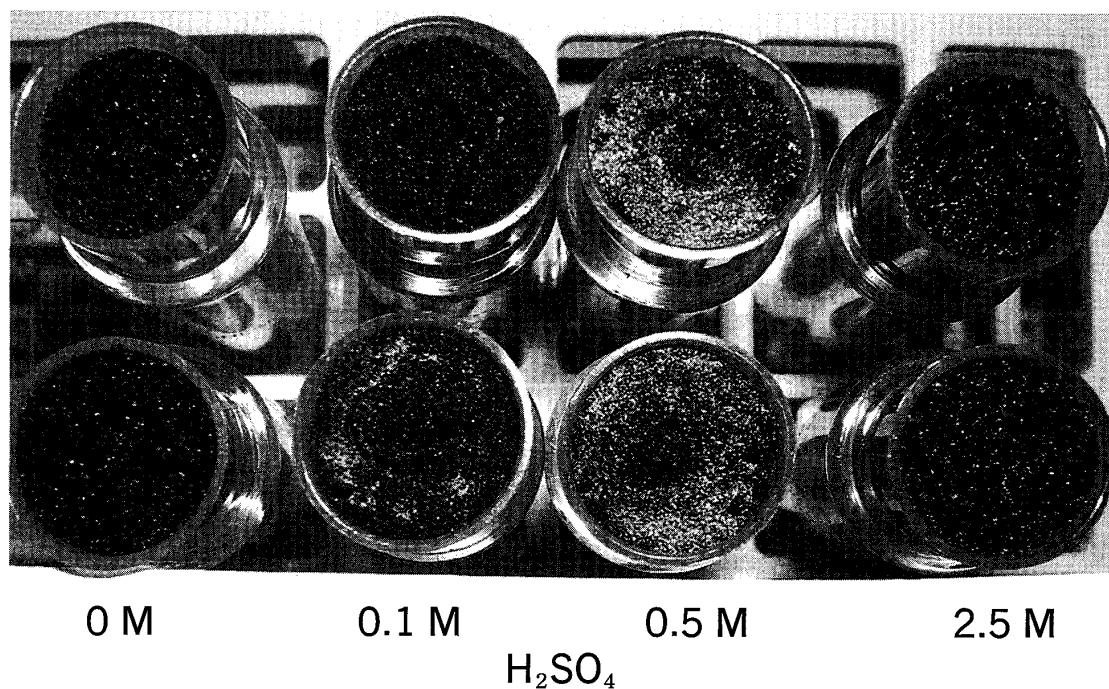


FIG. 4. Surfaces of crushed scoria with added 0, 0.1, 0.5, and 2.5 mol L⁻¹ H₂SO₄ on the 4th day after addition.

[Al₂(SO₄)₃ · 17H₂O]. The other set of diffraction peaks at 0.758, 0.426, 0.376, 0.305, etc., is attributable to CaSO₄ · 2H₂O. The diffraction peak at 0.902 nm may be due to iron sulfate or other materials. The final pH(H₂O) values of the scoria to which 0, 0.1, 0.5 and 2.5 mol L⁻¹ H₂SO₄ were added were 5.3, 3.1, 2.3 and 1.1, respectively, on the 4th day after addition. The initial pH(H₂O) values of the solutions were 5, 0.93, 0.43 and < -0.30, respectively, therefore, more than 90% of H⁺ reacted with the scoria during the period of 4 days. The solubility of alunogen is so high (38.5 g in 100 g of water at 25°C) that the diffraction peaks for alunogen disappeared from the XRD pattern after rinsing with water, whereas those for gypsum remained (Fig. 5e). The solubility of gypsum is 0.209 g as CaSO₄ in 100 g of water, much lower than that for alunogen.

The results from XRD analysis (Fig. 5) were supported by SEM-EDX analysis (Fig. 6). Fig. 6-i shows a SEM image of the crushed scoria with added water. Crushing exposed fresh surfaces of scoria particles in addition to somewhat altered surfaces possibly due to oxidation of hot scoria right after volcanic eruption and/or ordinary weathering. The EDX spectrum Fig. 6a indicates that Al, Si, Ca, and Fe are the major elements of relatively fresh scoria, and this elemental composition is close to those reported by Kato *et al.* (2005). Altered surfaces of scoria which showed a brown color under an optical microscope appears to indicate a high Fe concentration (Fig. 6b).

With the addition of 0.1 mol L⁻¹ H₂SO₄, prismatic gypsum (Fig. 6d) and

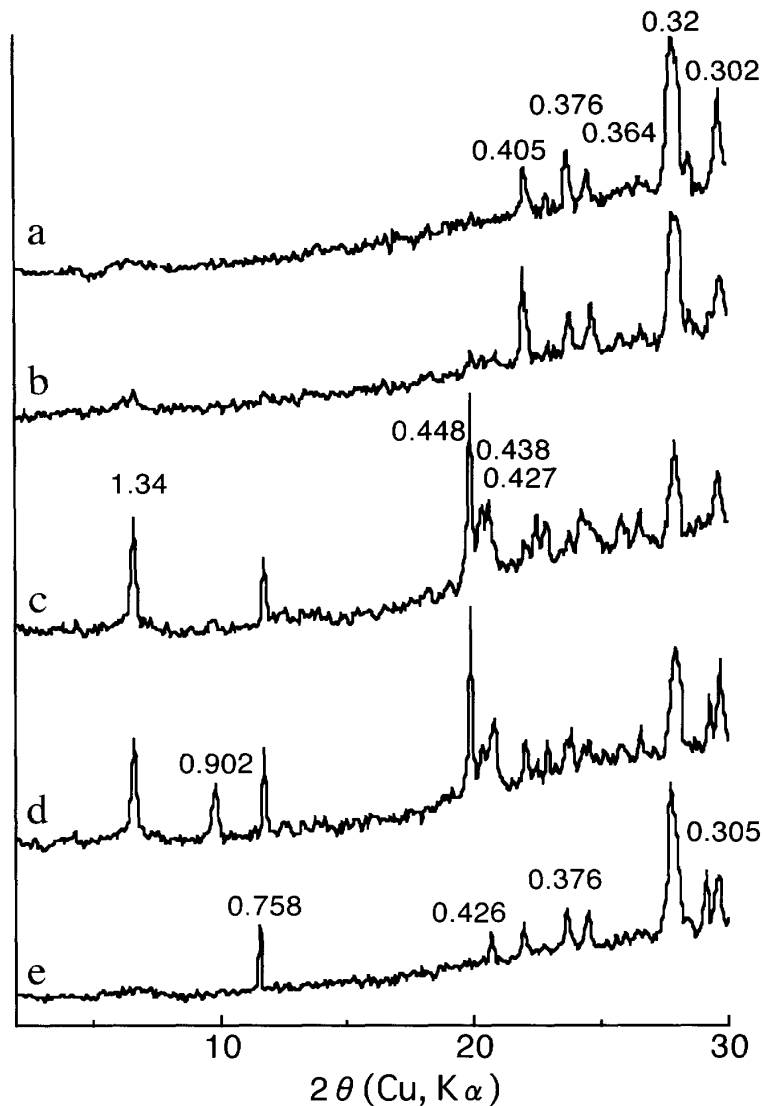


FIG. 5. X-ray diffraction (XRD) patterns of the reaction products between crushed scoria and 0 (a), 0.1 (b), 0.5 (c), or 2.5 (d) mol L⁻¹ H₂SO₄. e: XRD pattern of the reaction products between crushed scoria and 2.5 mol L⁻¹ H₂SO₄ after rinsing with water.

platy alunogen (Fig. 6e) were found on the surface of the fresh scoria (Fig. 6c). However, because the EDX spectrum of Fig. 6e shows that the S/Al atomic ratio of the platy crystal is larger than that for theoretical alunogen of 1.5, Al₂(SO₄)₃ · nH₂SO₄ · mH₂O may also be partly included. Alunogen (Fig. 6f) and gypsum (Fig. 6g) were also found in Fig. 6-iii and -iv which show the reaction products between scoria and 2.5 mol L⁻¹ H₂SO₄. Iron sulfate is also included in Fig. 6-iv. After rinsing with water, alunogen was removed and prismatic gypsum (Fig. 6-i) appeared more evident in Fig. 6-v than in Fig. 6-iv. In addition, a small amount of a Si-rich amorphous precipitate was also found in Fig. 6-v through EDX analysis (data not shown). Although the SEM image and EDX spectra for the

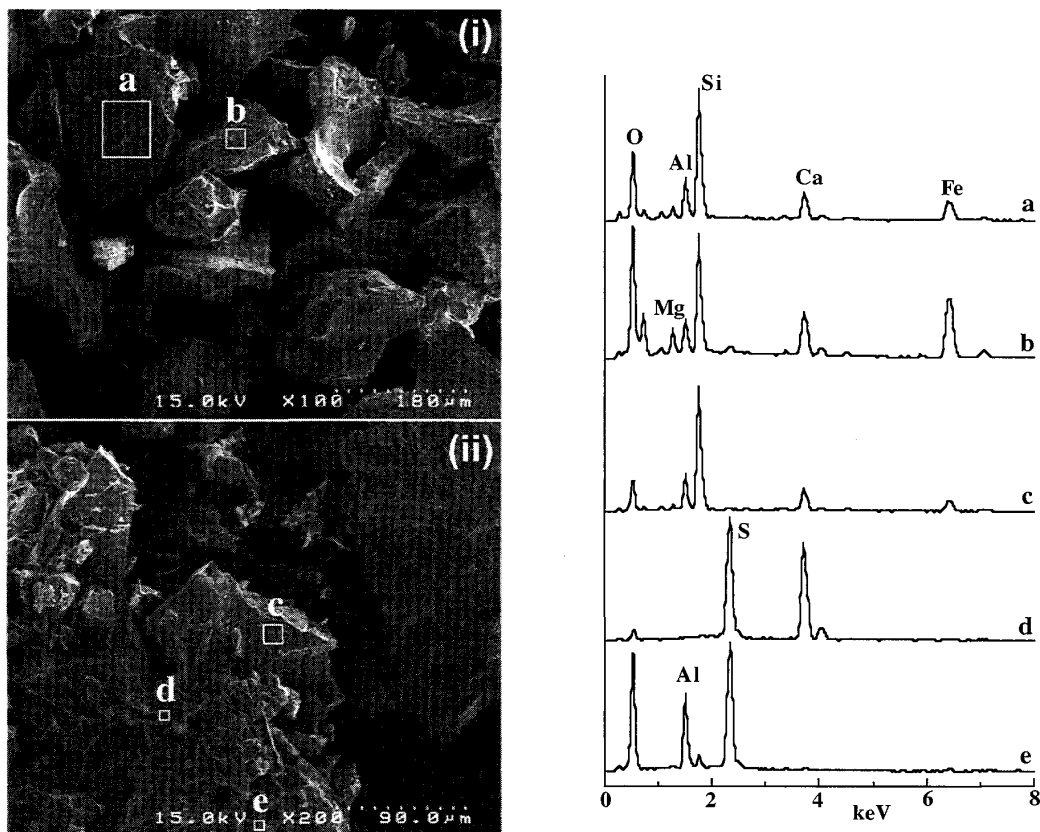


FIG. 6. (continued on next page)

reaction products between scoria and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ have been omitted from Fig. 6, alunogen and gypsum were also found in the product.

Comparison of WPM and reaction products between scoria and dilute H_2SO_4

The $\text{pH}(\text{H}_2\text{O})$ value of WPM was 4.1. This is lower than that of the crushed scoria and is higher than that for the reaction mixture between scoria and $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The $\text{pH}(\text{H}_2\text{O})$ values reported for new volcanic ash deposits on Miyake Island in 2000 range between 3.1 and 4.0 (Kato, *et al.*, 2002). These $\text{pH}(\text{H}_2\text{O})$ values are partly included in the $\text{pH}(\text{H}_2\text{O})$ range of the present laboratory experiment. The low $\text{pH}(\text{H}_2\text{O})$ of the 2000 ash was considered to be due to oxidation of sulfur (Yazawa *et al.*, 2004) as well as the effect of sulfur dioxide gas. The $\text{pH}(\text{H}_2\text{O})$ value decreased to 4.0 after storage of the ash for 2 years, although it ranged between 5.5 and 7.1 a few days after deposition (Yazawa *et al.*, 2002; Yazawa *et al.*, 2004).

As mentioned above, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was common to the WPM at the load-cut profile and to the reaction products between dilute sulfuric acid and scoria. A possible process for crystallization of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the WPM is the dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ contained in the overlying 2000 ash (Kato *et al.*, 2002; Yazawa *et al.*, 2003) or formed by the reaction of scoria with H_2SO_4 from the 2000 ash, and

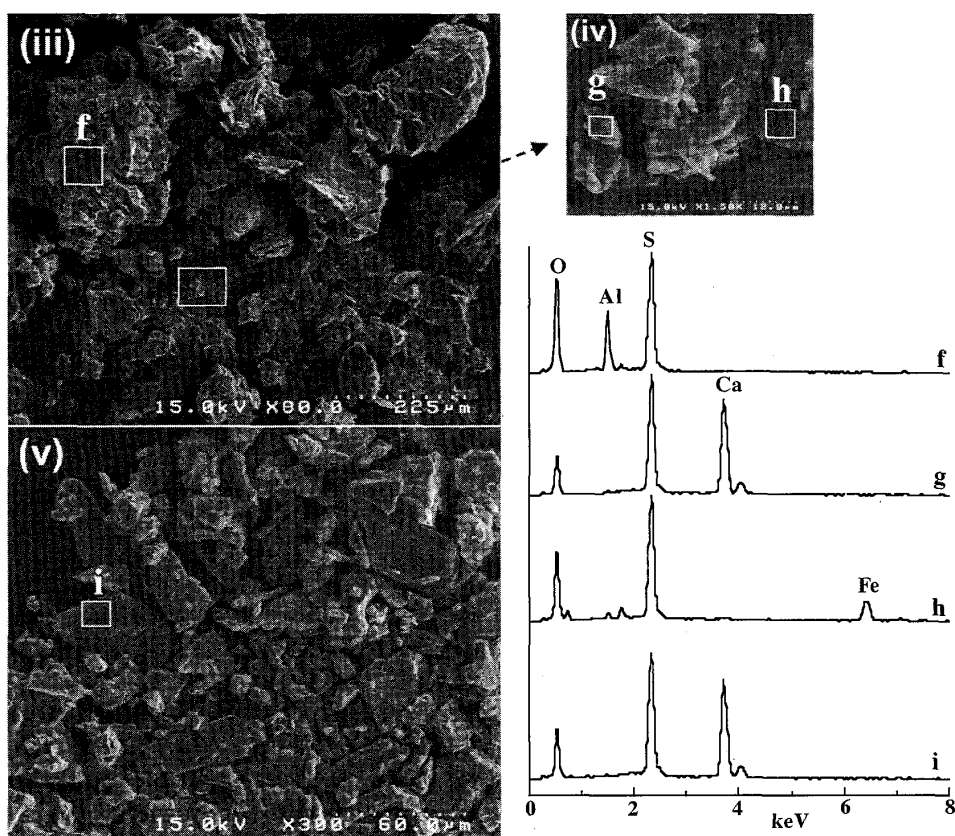


FIG. 6.

FIG. 6. Scanning electron microscope (SEM) images and energy dispersive X-ray (EDX) spectra of the reaction products between crushed scoria and 0 (i), 0.1 (ii), and 2.5 (iii) mol L⁻¹ H₂SO₄. iv: partly magnified image of iii. v: iii after rinsing with water and magnification. A, b, c, d, e, f, g, h and i show EDX spectra obtained from selected areas shown by a box having the same letter in SEM images.

its re-precipitation on the surface of the scoriaceous road-cut profile after a rainy season as an evaporite. If H₂SO₄ were formed from sulfur dioxide gas on the wet surface of the road-cut profile, it is also possible that CaSO₄ · 2H₂O was formed. Although the crystal size of CaSO₄ · 2H₂O was highly variable in the WPM of the road-cut profile, the crystals shown in Fig. 1-ii are much larger than those formed in the present laboratory experiment. The large CaSO₄ · 2H₂O crystals might have formed more slowly than in the present laboratory experiment. The white precipitate of amorphous silica in WPM also possibly originates from both scoria and the 2000 ash.

Alunogen was not found in the WPM of the road-cut profile. According to Horiguchi *et al.* (2000), alunogen crystallized in a dry season (October, 1992) on the walls of a tunnel dug in the sandy tuff of Yoshimi hill, Saitama Prefecture, Japan. However, it fell off and little was found on the walls in a wet season (July, 1993). Alunogen can be washed away or scarcely crystallized in a large

amount of rainwater, considering the high concentrations of Al and SO_4^{2-} in the water extract of volcanic ash deposits in 2000 (Kato et al., 2002). BAS was not found as one of major constituents either in the WPM in the road-cut profile or in the reaction products between scoria and dilute H_2SO_4 . BAS may form in a partial neutralization process of alunogen.

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